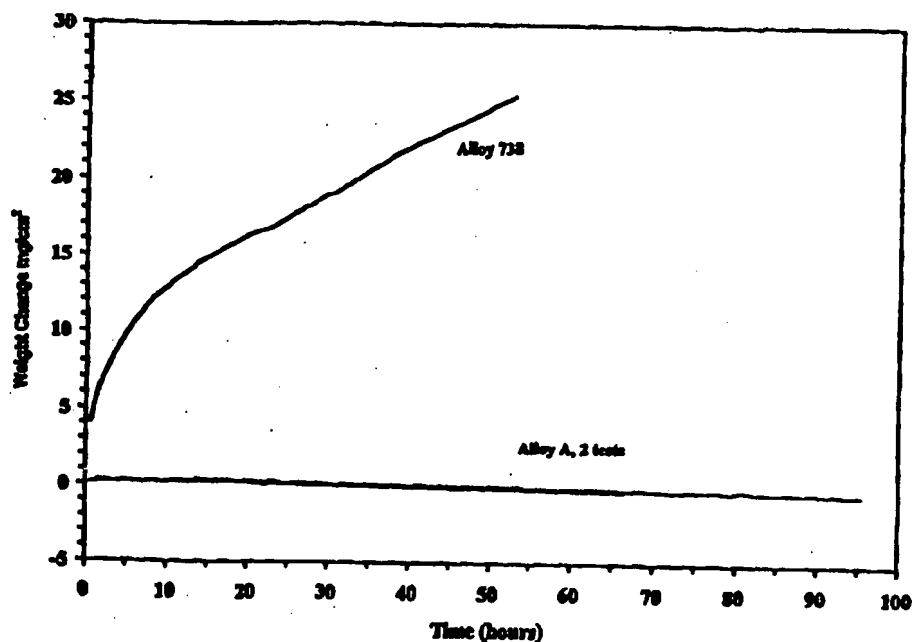




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁶ : C22C 5/04, 19/03, 19/05, 19/07, 30/00, 38/08, 38/10, 38/12, 38/14, 38/18, 38/22, 38/24, 38/26, 38/28, 38/30, 38/32, 38/40, 38/44, 38/46, 38/48, 38/50, 38/52, 38/54</p>	A1	<p>(11) International Publication Number: WO 97/38144</p> <p>(43) International Publication Date: 16 October 1997 (16.10.97)</p>
<p>(21) International Application Number: PCT/US97/05974</p> <p>(22) International Filing Date: 10 April 1997 (10.04.97)</p> <p>(30) Priority Data: 08/630,812 10 April 1996 (10.04.96) US</p> <p>(71) Applicant: THE PENN STATE RESEARCH FOUNDATION [US/US]; 304 Old Main, University Park, PA 16802 (US).</p> <p>(72) Inventors: SIMKOVICH, George; 841 Oak Ridge Avenue, State College, PA 16802 (US). WHITNEY, Eric, J.; 712 Sunset Road, State College, PA 16803 (US).</p> <p>(74) Agent: MONAHAN, Thomas, J.; The Pennsylvania State University, Intellectual Property Office, 113 Technology Center, University Park, PA 16802 (US).</p>		<p>(81) Designated States: AU, CA, JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published With international search report.</p>

(54) Title: IMPROVED SUPERALLOYS WITH IMPROVED OXIDATION RESISTANCE AND WELDABILITY



(57) Abstract

Improved Ni, Fe and Co based superalloys having excellent oxidation resistance and weldability are disclosed. The superalloys are obtained by at least partially replacing the Ni in conventional superalloys with from 2-55 % of Pd, so that for example the total weight-% of Ni+Pd is in the range of 50-80 %; or Ni+Pd+Fe, 50-80 %. The alloys may also contain strengtheners and modifiers such as Co, W, Mo, V, Ti, Re, Ta, Nb, C, B, Zr, Y, and Hf. The superalloy has good strength, improved weldability, and excellent oxidation resistance suitable for use in many aerospace and power generation turbine applications.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Improved Superalloys With Improved Oxidation Resistance And Weldability

GOVERNMENT SPONSORSHIP

This invention was made with Government support under Contract Number N00039-
5 92-C-0100 awarded by the United States Department of the Navy.. The Government has
certain rights in this invention.

FIELD OF THE INVENTION

The present invention relates to the field superalloys containing palladium. The
invention is particularly drawn to nickel-based superalloys useful in aerospace and power
10 generation turbine applications. The superalloy's weldability, strength and excellent oxidation
resistance properties make it useful in turbine blade tip manufacturing or refurbishment as well
as in other high temperature components such as combustors, nozzles, flame holders and seals
where these properties are desirable or critical.

BACKGROUND OF THE INVENTION

The term "superalloy" is used to represent complex nickel, iron, and cobalt based
alloys containing additional metals such as chromium, aluminum, titanium, tungsten, and
molybdenum. These additives are used for their high values of mechanical strength and creep
resistance at elevated temperatures and improved oxidation and hot corrosion resistance. For
20 nickel based superalloys, high hot strength is obtained partly by solid solution hardening using
such elements as tungsten or molybdenum and partly by precipitation hardening. The
precipitates are produced by adding aluminum and titanium to form the intermetallic
compound γ' , based on $\text{Ni}_3(\text{Ti}, \text{Al})$, within the host material.

The properties of superalloys make them desirable for use in corrosive and/or
25 oxidizing environments where high strength is required at elevated temperatures. Superalloys
are especially suitable for use as material for fabricating components such as blades, vanes,
etc., for use in gas turbine engines. These engines usually operate in an environment of high

temperature and/or high corrosiveness. Therefore a need exists for alloys with high temperature oxidation resistance and/or good hot corrosion resistance.

Nickel based superalloys are well known in this field. For instance, U.S. Patent 4,261,742 to Coupland et al. discloses a superalloy consisting essentially of 5 to 25 wt % chromium, 2 to 7 wt % aluminum, 0.5 to 5 wt % titanium, at least one of the metals yttrium and scandium present in a total amount of 0.01 to 3 wt %, 3 to 15 wt % in total of one or more of the platinum group metals, and the balance nickel. The Coupland et al. superalloy has increased oxidation and hot-corrosion resistance and may be used as a material for fabricating blades or vanes of gas turbine engines or components used in coal gasification systems. Also, U.S. Patent 4,018,569 to Chang discloses an alloy consisting essentially of 8 to 30 wt % aluminum, 0.1 to 10 wt % hafnium, 0.5 to 20 wt % of an element selected from the group consisting of platinum, rhodium and palladium, 0 to 3 wt % yttrium, 10 to 40 wt % chromium, and the balance comprising an element selected from the group consisting of iron, cobalt and nickel. The Chang superalloy has improved environmental resistance which may be used to improve the temperature capability of components in gas turbine engines. However, neither Coupland et al. nor Chang disclose superalloy compositions containing palladium in amounts sufficient to improve the weldability of the superalloy in accordance with the requirements of the present application. These patents are hereby incorporated by reference.

Other patents are known that disclose high temperature nickel containing alloys.

Some examples include: U.S. Patent 4,149,881 to D'Silva, U.S. Patent 4,414,178 to Smith, Jr. et al., U.S. Patent 4,719,081 to Mizuhara, and U.S. Patent 4,746,379 to Rabinkin hereby incorporated by reference. These patents disclose alloys with various amounts of palladium, chromium and nickel but do not contain aluminum which is a required element of the present invention.

Current and the next generation turbofan turbine engines use nickel based superalloys for many of the components in the high temperature sections of an engine. These sections include the later stages of the high pressure compressor, the combustor, the high and low pressure turbine, and the exhaust modules. These components are subjected to a wide variety of service related degradation including oxidation, fatigue, creep, corrosion, and erosion. In nearly all applications more than one of these phenomena occurs during turbine engine

operation. As a result, alloy design principally has been concerned with improving the thermomechanical properties of the alloys. Produceability of the alloy, i.e., weldability, castability, forgeability, and machineability are often considered a secondary or tertiary criterion during alloy design. However, when weldability is considered during alloy design the resulting material may be widely used. For example, Alloy 625 and its derivatives (including Alloy 718) are the most widely used superalloys in the world [H. L. Eiselstein and D. J. Tillack "The Invention and Definition of Alloy 625", *Superalloys 718, 625 and Various Derivatives*, Conference Proceedings, Pittsburgh Pa., June 1991, ed. E. A. Loria].

To improve the oxidation resistance and strength of Ni alloys, successive generations of alloys have incorporated increasingly higher levels of aluminum and to a lesser extent titanium. Both Al and Ti are detrimental to weldability.

There are several modes of cracking that can occur during welding. One of the most troublesome is strain age cracking of the weld metal or in the heat affected zone of the base material. Strain age cracking is the principal reason why nickel based superalloys are considered to be difficult to weld [*Welding Handbook* Vol. 4, Seventh Edition, ed. by W.H. Kearns, p. 233 and 236, © 1982 American Welding Society]. This type of cracking can occur during cooling from weld temperature, during post weld heat treatment, or during the application of subsequent weld passes. The primary reason these alloys exhibit strain age cracking is that the aging kinetics of the γ' phase is very fast and the alloy can not accommodate the resulting strain without cracking. Figure 1 shows the relationship between an alloy's Al + Ti content and weldability [M. Prager and C. S. Shira, *Weld. Res. Council. Bul.*, 128, 1968]. Note that alloys containing greater than 3% Al are considered difficult to weld, in addition as Ti levels increase the allowable amount of Al present in the alloy also decreases. For alloys that lie close to the line, such as Rene'41 and Waspaloy, special heat treatments have been used to reduce cracking. For example, over aging Rene'41 has been shown to reduce strain age cracking through the coarsening of the γ' phase [W. P. Hughes and T.B. Berry, "A Study of the Strain-Age Cracking Characteristics in Welded Rene'41-Phase 1", *Welding Journal*, Aug. 1967, p 361-370].

It is common for current generation superalloys to have as much as 12% Al with little or no Ti present. The impossibility of welding these alloys has a significant impact on the

repairability of components made from such alloys. For example, a turbine blade may be removed from service due to tip wear while the component still has a significant portion of its design life remaining. It is desirable to weld repair the worn area and return the component to service. Currently these components are repaired using a solid solution strengthened alloy
5 such as Alloy 625, Hastelloy X, L605, or HS188. However, these alloys lack the strength and oxidation resistance of the original material; as a result the repaired components suffer rapid degradation during subsequent service.

Several other types of cracking can occur in superalloy weldments. For castings and large grain wrought materials grain boundary liquation cracking or hot shortness may occur.

10 This type of cracking is minimized by using a low heat input process such as laser, electron, or micro plasma arc welding and controlling the level of carbide forming and impurity elements [T.J. Kelley, "Welding Metallurgy of Investment Cast Nickel-Based Superalloys", *Weldability of Materials*, Conference Proceedings, ed. R.A. Patterson and K.W. Mahin, ©1990 ASM International]. Also, weldments can also suffer from nil ductility cracking and restraint
15 cracking. Both of which are best minimized by proper weld schedule development and process control.

Current generation Ni based superalloys derive their oxidation resistance from the formation of an extremely adherent and cohesive Al_2O_3 surface layer. The formation of the Al_2O_3 film depends on the Al content of the alloy and other elements such as Cr, Y, Hf, and Ti
20 [C. T. Sims and W. C. Hagel, eds., The Superalloys, © 1972 Wiley, NY]. However, increasing aluminum content is the most effective method of improving oxidation resistance. Increasing the aluminum content is limited by the need to balance other thermomechanical properties. As a result oxidation resistant coatings have been developed to increase the Al content at the surface. One technique is to apply a diffusion aluminide coating where Al is
25 applied by a pack cementation or a chemical vapor deposition process. Other coating systems are based on the MCrAlX (M can be Ni and/or Co and X can be Y and/or Hf) alloys. These alloys are similar to superalloys except they are very high in Al and contain as much as 1.5% Y or Hf. These coatings are applied by physical vapor deposition or a thermal spray process. One variation of the above coating is to electroplate onto the surface of a component Pd to
30 improve the oxidation and corrosion resistance [S. Alperine, P. Steinmetz, A. Friant-

Costantini, P. Josso, "Structure and High Temperature Performance of Various Palladium-Modified Alumined Coatings: A Low Cost Alternative to Platinum Aluminides," *Surface and Coating Technology*, 43/44 (1990), 347-358; P. Lamesle and P. Steinmetz, "Growth Mechanisms and Hot Corrosion Resistance of Palladium Modified Aluminide Coatings on Superalloys", *Materials and Manufacturing Processes*, vol. 10, no. 5, 1053-1075, (1995)].

At Penn State, work has been performed studying the effects of Pd on the oxidation behavior of Mo-Cr and Mo-W-Cr alloys [D. Lee and G. Simkovich, "Oxidation of Molybdenum-Chromium-Palladium Alloys," *Oxidation of Metals*, 34, Nos. 1/2, (1990); D. Lee and G. Simkovich, "Oxidation of Mo-W-Cr-Pd Alloys," *Journal of Less Common Metals*, 163 (1990), 51-62]. The results show that 1-3 wt. percent Pd is sufficient to significantly improve the high temperature oxidation resistance of the alloy systems. The researchers hypothesized that Pd acts as a Cr reservoir for the formation of Cr_2O_3 and as a barrier to the inward diffusion of oxygen. There have not been previous studies on the effects that Pd additions have on the oxidation resistance of Ni based superalloys.

Previous work on platinum additions to superalloys has shown a beneficial effect on oxidation behavior at high temperature. Platinum concentrations of about 1-3 weight percent were shown to significantly reduce the high temperature oxidation rate of the base metal. The improvement was attributed to an increase in the diffusion rate of other species [I. M. Allam, H. C. Akuezue, and D. P. Whittle, "Influence of Small Pt Additions on Al_2O_3 Scale Adherence", *Oxidation of Metals*, Vol. 14, No. 6, 1980]. This may be due to an increase in lattice parameter of the γ phase caused by the presence of Pt. In the presence of Hf, Pt promotes inwardly growing Al_2O_3 pegs that reportedly increased scale adherence [G. J. Tatlock and T. J. Hurd, "Platinum and the Oxidation Behavior of a Nickel Based Superalloy", *Oxidation of Metals*, Vol. 22, Nos. 5/6, 1984]. It is possible that Pd additions may also increase oxide scale adherence by the same or other mechanisms.

The surface segregation of Cr, Pd, Mo, and N for a high chromium ferritic stainless steel has been studied [W. E. Delport and J. P. Roux, "The Surface Segregation and Oxidation of Chromium and Palladium in High Chromium Stainless Steels", *Corrosion Science*, Vol. 26, No. 6, pp. 407-417, 1986]. The investigators found that at 550 °C palladium oxidation is virtually complete before the oxidation of chromium begins. Also, the data suggests that Cr

diffuses more rapidly through PdO than through the bulk material. This data suggests that the passivation characteristics of a ferritic stainless steel would be improved if a small amount of palladium (approximately 0.4 weight percentage) is added to the steel. Unfortunately, the study did not investigate high temperatures, where the formation of PdO can not occur.

5 Gas turbine engines are used in a wide variety of applications including commercial and military aircraft and for electrical power generation. Fuel efficiency is a major concern for turbine manufacturers and operators. Considerable effort is expended during the design of turbines to improve fuel efficiency over earlier models, and operators spend a large part of their maintenance effort to maintain fuel efficiency. Fuel represents a major cost for both
10 airlines and electric utilities.

Fuel efficiency is increased over earlier engines by incorporating new designs that take advantage of advances in aerodynamics and computer simulation. Fuel efficiency is also increased by incorporating advanced materials that allow the engine to operate at higher combustion temperatures. Higher combustion temperature results in more complete burning
15 of the fuel. New materials are usually more expensive due to an increase in raw material and manufacturing costs. Often these costs are more than offset by a decrease in fuel costs. Superalloys have been used extensively in the hot sections of turbine engines because of their high strength and excellent resistance to oxidation (usually with the addition of a coating). Unfortunately superalloys are very difficult to fusion weld. The inability to fusion weld
20 superalloys results in increased new part manufacturing cost and an increase in maintenance costs. It is desirable to develop a new alloy that has both excellent oxidation resistance and is more weldable than current alloys.

Turbine efficiency is reduced when excessive clearances develop between rotating components and stator components. In the turbine, unwanted clearances develop due to the
25 thermomechanical degradation of the blade tip allowing airflow to leak past the blades. Often turbine blade tip degradation becomes severe enough for the operator to remove the blade from service for repair. The repair consists of welding a sufficient amount of repair material to the tip and recontouring the blade to final dimensions. The repair material is often Alloy 625. This material is a solid solution strengthened nickel alloy that has inferior oxidation
30 resistance to the original blade material. However, Alloy 625 exhibits excellent weldability

compared to most original blade materials which have such poor weldability that they can not be used as the repair material.

Because most repair material, frequently Alloy 625, has poor oxidation resistance, it does not maintain clearances and causes the turbine blades to be removed frequently for additional repairs. By substituting Alloy 625, or other repair material, with the subject invention, the turbine operator will realize a reduction in fuel consumption and maintenance costs

SUMMARY OF THE INVENTION

Accordingly, there is a need for a new alloy that provides for improved weldability while maintaining the oxidation resistance similar to that of traditional superalloys. The present invention is a new superalloy with improved weldability, excellent oxidation resistance and strength adequate for aerospace and power generation turbine applications. The alloy derives improved weldability from the addition of palladium. It is preferred that the palladium replace existing Ni in conventional nickel-based superalloys. The palladium also improves high temperature oxidation resistance and provides solid solution strengthening.

Palladium additions may improve weldability via four mechanisms: (1) Pd increases aluminum solubility in the system resulting in a decrease in the volume fraction of γ' , (2) Pd may decrease the γ' solvus temperature, increase the γ' coarsening rate and reduce strain age sensitivity, (3) Pd may delay the onset of γ' precipitation during post weld cooling, and (4) Pd may increase lattice mismatch in the presence of a species that exclusively substitutes for aluminum in γ' . The palladium additions may improve oxidation via the following mechanisms: (1) Pd will increase the aluminum solubility in the system resulting in more Al available to form an oxide scale, (2) a Pd enriched layer will form near the surface increasing the diffusion distance for other elemental constituents, and (3) Pd may inhibit the diffusion of oxygen into the substrate thereby reducing internal oxidation.

One intended use for the alloy is as a filler metal for turbine blade tip manufacturing or refurbishment. Currently, there is no superalloy tip material being used as a refurbishment material. Other high temperature components such as combustors, nozzles, and seals can also be welded (for new part or refurbishment) using the new alloy.

Another use of the alloy would be structural components of a turbine engine, particularly components that require excellent oxidation resistance and may require repair during the life time of the component. Such a repair may involve welding to restore dimensional and structural integrity to the part. It would be important in such a repair that welding does not induce cracks that may promote early and potentially catastrophic failure.

For the purposes of this invention disclosure the term 'welding' refers to a fusion weld process with or without a filler material. This type of welding can be performed when dimensional restoration is required or when piece parts are joined to form an inseparable assembly.

When used as a repair material for turbine blade tips the new alloy will save energy by reducing the amount of degradation in efficiency due to normal operation of a gas turbine (i.e., the turbine will maintain its designed efficiency for longer periods of time). Energy will also be saved by allowing the design of turbines with improved efficiency over those currently available. There is potential to significantly increase the savings by incorporating the new alloy into more than one application. Further, energy savings may be realized when the new alloy is used in other applications in a turbine.

The new alloys of the present invention provide for weldable oxidation resistant superalloys that are currently unavailable. The alloy will allow jet engine manufacturers and overhaulers to provide improved components at a manufacturing cost similar to current repair techniques. In addition it will allow components to be repaired using existing processes. It will also allow the repair of components with similar oxidation resistance as the original material so no loss of performance is experienced.

The alloys represent a departure in design philosophy usually employed in the development of superalloys. Typically weldability is not a design criterion. In this approach weldability and oxidation are primary design criteria along with elevated temperature mechanical properties. It is believed that the palladium additions will help to achieve the design goals.

These and other advantages of the present invention are accomplished by either replacing nickel with palladium in an existing superalloy or by designing new alloys with palladium as a major alloying constituent. The new alloy can be based on conventional nickel,

iron, or cobalt based materials, including superalloys. Further, the new alloy may be an enhancement to mechanically alloyed or aluminide classes of materials.

BRIEF DESCRIPTION OF THE DRAWINGS

5 Figure 1 is a graph showing the weldability as a function of aluminum and titanium content in alloys that do not contain palladium [not the present invention].

Figure 2 is a graph showing the effect of solute concentration on the lattice parameter of gamma nickel.

Figure 3 shows the effect of solute concentration on the lattice parameter of Ni_3Al .

10 Figure 4 shows 1150°C isothermal oxidation results for the alloys listed in table 5.

Figure 5 shows 1200°C isothermal oxidation results for the alloys listed in table 5.

Figure 6 shows the 1150°C isothermal oxidation results for three alloys with equivalent solute contents and varying Pd amounts

DETAILED DESCRIPTION OF THE INVENTION

15 Pd is a face centered cubic metal and exhibits complete substitutional solid solubility with Ni [Metals Handbook, Vol. 8, 8th Ed., © American Society for Metals, 1973; Binary Alloy Phase Diagrams, Vol. 3, 2nd Ed., T. B. Massalski Ed., © ASM Int., 1990]. However, Pd has a higher solid solubility for Al. For example, Ni has an Al solubility at 1000 °C of 14 atomic percent while Pd at the same temperature has an Al solubility of 20 atomic percent.

20 Similarly, at 800 °C the Al solubility in Ni and Pd is 10 and 17 atomic percent respectively.

There is no Al-Pd-Ni ternary phase diagram available, a review of the binary phase diagrams shows that there is a Pd-Al eutectic at approximately 23 atomic percent Al that melts at 1055 °C. In the Ni-Al system there is a eutectic at approximately 13 atomic percent Al that melts at 1385 °C. As a result it may be expected that a ternary eutectic may exist in
25 the 13-23 atomic percent region and may have a melting point between 1055°C and 1385°C. From this information it can be hypothesized that the γ' aging kinetics may be favorably influenced, i.e., decreasing γ' precipitation rate with the addition of Pd. This would have a

favorable impact on a weld to resist strain age cracking either occurring during post weld heat treatment or in the weld bead during subsequent weld passes.

Table 1 shows the relevant crystallographic data for Ni Pd, and Al. Note that the atomic radius and lattice constant are more closely matched for Pd and Al than for Ni and Al.

- 5 According to alloying rules first proposed by Hume-Rothery, the closer the match between atomic radii the higher the solubility of the solute [Physical Metallurgy Principles, Second Edition, by Robert E. Reed-Hill, ©1973 Litton Educational Publishing Inc.]. This criterion, known as the size factor, states that atomic radii differences of less than 15% can result in substantial solid solubility. This limitation is associated with the strain induced by the solute
- 10 atoms in the lattice. Note that the difference between Ni and Al is 13% while the difference between Pd and Al is only 4%. This supports the conclusions reached by inspection of the phase diagrams.

Table 1: Crystal Structure Of Ni, Pd, and Al

Element	Crystal Type	Atomic Radius	Lattice Constant
Ni	FCC	1.246	a=3.5238
Pd	FCC	1.376	a=3.8902
Al	FCC	1.432	a=4.0391

values given in angstroms

15

The change in γ and γ' lattice parameters as a function of alloying element has been studied previously [M. Yoshinai, O. Shouichi, and T. Suzuki, "Lattice Parameters of Ni(γ), Ni₃Al(γ'), and Ni₃Ga(γ') Solid Solutions with Additions of Transition and B-Subgroup Elements", *Acta Metallurgica*, Vol. 33, No. 6, pp. 1161-1169, 1985, © 1985 Pergamon Press

20 Ltd.]. Figure 2 shows the effect of solute concentration on the lattice parameter of gamma nickel. Palladium has a significant effect on the γ' lattice parameter, of the elements shown only Nb and Ta have a larger effect. Note that the solubility limit of each element has not been accounted for in the figure.

Figure 3 shows the effect of solute concentration on the lattice parameter of Ni₃Al. Pd

25 has a large effect on the Ni₃Al lattice parameter. Pd replaces Ni in γ' and in a ternary Ni-Pd-

Al systems partitions equally between γ and γ' . This results in little net change in the lattice mismatch between γ and γ' .

The alloying behavior of a variety of Ni_3X (X can be Al, Ga, Si or Ge) compound has been investigated [S. Ochiai, Y. Oya, T. Suzuki, "Alloying Behavior of Ni_3Al , Ni_3Ga , Ni_3Si and Ni_3Ge ", *Acta Metallurgica*, Vol. 32, 289, 1984, © 1984 Pergamon Press Ltd.].

Palladium was shown to substitute exclusively for nickel. At 1050°C Pd has a solubility in γ' of approximately 15 atomic percent. In superalloys, cobalt is the only other common element that was shown to substitute for nickel, however its γ' solubility decreases with increasing temperature. Most other elements partition to Al sites or will substitute for both Ni and Al.

For example, Ti and Nb will partition to the γ' Al sites and result in an increase in lattice parameter mismatch. Cr will partition to either Ni or Al sites, however Al sites are more likely to be occupied by Cr.

The addition of palladium will not promote the formation of topologically close packed phases such as σ , μ , or Laves. This is because palladium has nearly the same electron hole number as nickel (0.61 for nickel compared to approximately 0.66 for palladium) [Heat Treatment Structure and Properties of Nonferrous Alloys by C. R. Brooks, © 1984 American Society for Metals, p. 199]. As a result, PHACOMP calculations yield about the same electron hole numbers for alloys with nickel or palladium. The formation of TCP phases is not a problem when substituting Ni with Pd in existing superalloys.

It is difficult to predict the effect palladium will have on the lattice parameter mismatch, γ' solvus temperature, γ' coarsening rate, Pd partitioning, aluminum solubility, the formation of other Pd bearing intermetallics, and the role Pd has in oxidation. However, the information taken from various binary and ternary systems indicates that palladium can favorably impact weldability and oxidation resistance.

If palladium partitions equally between γ and γ' , then there would be little effect on the hardening affect of the γ' ; however, the increase in aluminum solubility should reduce the total volume fraction present at any given temperature. If Pd does not partition equally, then the lattice mismatch will increase and the hardening affect of the γ' will decrease.

Because of the high solubility of Al in Pd and the presence of a low melting point Al-Pd eutectic a decrease in the γ' solvus may occur in complex alloys. This would delay the onset of γ' precipitation during cooling from welding temperatures. The strains induced by cooling may be more easily accommodated. Also, the lower solvus temperature would put
5 more aluminum into solution at operating temperature.

Although the beneficial effect of Pt on oxidation resistance has been shown, there are no documented studies on the effect of Pt on weldability. This is probably because the Pt levels were thought to be too small to have a measurable affect on weldability. More importantly, weldability was not a concern for the alloy designers investigating Pt additions to
10 superalloys.

A review of the Pt-Al phase diagram shows that Pt has less solubility for aluminum at 1000 °C than either Ni or Pd at the same temperature [P.R. Hultgren, *Selected Values of Thermodynamic Properties* Supp. 1, part 1, Alloys, © 1963 John Wiley & Sons]. As a result, the solubility of Al in γ would not increase. This would effectively result in little or no
15 reduction in γ' volume fraction. Since platinum is also likely to partition equally between γ and γ' there would be no net increase in lattice mismatch.

A necessary condition for a species to improve weldability is that it must replace exclusively Ni in γ' and its solubility for aluminum must be greater than that of nickel. Pt does not meet the second condition. Palladium, however, appears to meet the necessary conditions
20 to improve both oxidation and weldability.

Example 1

To improve the weldability and oxidation resistance of an existing superalloy it is proposed to substitute approximately half of the nickel by weight with palladium. The exact level of substitution will be dictated by the amount of Pd necessary to improve weldability. It
25 is likely that the higher the Al + Ti percentage in the alloy the higher the concentration of Pd necessary to make a noticeable improvement in weldability. Once the substitution is made the weight percent of the other constituents would be adjusted to maintain the same atom proportions as the original alloy. The following example given in Tables 2 and 3 illustrates the

technique for IN738 alloy [Superalloys A Technical Guide, ed. E. F. Bradley, © 1988 ASM International].

Table 2: Nominal Composition of IN738

	C	Ni	Cr	Co	Mo	Al	B	Ti	W	Zr	Ta	Nb
w%	0.17	61.3	16	18.5	1.75	3.4	0.01	3.4	2.6	0.1	1.75	0.9
a %	0.8	59.1	17.4	18.2	1.0	7.1	0.05	4.0	0.80	0.06	0.91	0.55

Table 3: Nominal Composition of IN738 with Pd Additions

	C	Ni	Pd	Cr	Co	Mo	Al	B	Ti	W	Zr	Ta	Nb
w %	0.15	36.7	30	13.8	7.4	1.5	2.9	0.01	2.9	2.3	0.09	1.5	0.78
a %	0.8	40.7	18.4	17.4	8.21	1.0	7.1	0.05	4.0	0.80	0.06	0.91	0.55

The amount of Pd necessary to make a noticeable improvement in IN738 weldability must be determined experimentally. Once the Pd level has been determined then other thermomechanical, oxidation and corrosion properties must be determined to establish suitability for a particular application.

In order to minimize the amount of Pd necessary to achieve the desired properties a new alloy has been designed. Design criteria for the new alloy are to maximize weldability and oxidation resistance while maintaining other properties, such as creep and rupture, at levels that would meet an intended application. For example, turbine blade tip repair requires that the tip possess a minimum rupture strength and some resistance to thermomechanical fatigue. The present inventors have established a base alloy on which other alloys can be designed to meet particular needs. The alloy consists of Ni, Pd, Cr, and Al. Other elements may be added to increase various thermomechanical properties. Table 4 shows the limits on the base alloy. It is preferred that the total wt % of Ni + Pd or of Ni + Pd + Fe (if Fe based) lies within the range of 50-80.

Table 4: Limits on Ni Superalloy with Pd

ELEMENT	WEIGHT PERCENT
Nickel	balance
Palladium	0.5 to 50
Chromium	0.5 to 30
Aluminum	0.5 to 20

Solid solution strengtheners such as Co, W, Mo, V, Ti, Re, Ta, Nb are added to improve tensile strength. Gamma prime modifiers such as W, Mo, V, Ti, Ta, and Nb are added to improve alloy strength and creep resistance, especially after an aging treatment.

- 5 Grain boundary strengtheners such as C, B, and Zr are added to reduce grain boundary sliding that may occur during creep. Finally, Y and Hf are added to improve oxidation behavior, if necessary.

Example 2

- 10 To improve the weldability and oxidation resistance of existing superalloys it is proposed to add palladium to the system. Table 5 shows the composition of a test alloy that was based on Alloy 738. In the test alloy, indicated by Alloy A, Pd simply added to the base alloy in an amount necessary to achieve approximately 20 atomic percent palladium. All other atom fractions of all other constituents were then reduced.

15

Table 5

	Elements (atomic percent)												
	Al	B	C	Co	Cr	Mo	Nb	Ni	Pd	Ta	Ti	W	Zr
Alloy 738	6.92	0.06	0.47	8.01	17.22	1.02	0.57	59.81	0.0	0.92	4.16	0.8	0.04
Alloy A	5.52	0.05	0.43	6.42	13.82	0.81	0.45	48.05	19.78	0.73	3.31	0.6	0.03

Figure 4 shows 1150°C isothermal oxidation results for the alloys listed in table 5. Note that the base alloy Alloy 738 oxidizes at a significantly faster rate than Alloy A, despite the reduction of Cr and Al in Alloy A due to the addition of Pd.

Example 3

To improve the weldability and oxidation resistance of an existing superalloys it is proposed to substitute nickel with palladium in such a way as to maintain the atom fractions of all other elements in the alloy. This can be accomplished by setting the Ni + Pd combined atom fraction to a level equal to the atom fraction of Ni in the base alloy. This technique is illustrated in Table 6. The atomic percentage of Ni in unmodified Alloy 738 is nominally 67.70. By adding palladium and keeping the Ni + Pd level equal to 67.70 then the atom fraction of the remaining constituents will remain unchanged.

Table 6 Constant Atomic Percentage of Solute

	Elements (atomic percent)												
	Al	B	C	Co	Cr	Mo	Nb	Ni	Pd	Ta	Ti	W	Zr
Alloy C	5.56	0.05	0.43	6.43	13.82	.82	0.45	62.68	5.02	0.74	3.34	0.63	0.03
Alloy B	5.56	0.05	0.43	6.43	13.82	.82	0.45	57.70	10.00	0.74	3.34	0.62	0.03
Alloy A	5.52	0.05	0.43	6.39	13.74	.81	0.45	48.12	19.78	0.73	3.31	0.62	0.03

Figure 6 shows the 1150°C isothermal oxidation results for three alloys with equivalent solute contents and varying Pd amounts. Note that as Pd levels increase the oxidation rate and total weight gain decreases. The exact level of palladium substitution will be dictated by the amount of palladium necessary to achieve improved weldability and sufficient oxidation resistance, which is determined experimentally.

Example 4

The design and of a new alloy that maximizes the benefits of the addition of palladium to a superalloy may be the best approach for newly design components or redesign of existing components. The design of a new alloy requires knowledge of the intended application or applications. For gas turbine operating temperatures between about 430°C and about 980°C

hot corrosion may be dominating mechanism of metal attack. Therefore a newly designed alloy for this temperature range must be resistant to hot corrosion. Typically chromium is added to alloys to increase hot corrosion resistance via the formation of a Cr_2O_3 scale. To improve weldability of these alloys, palladium is added in an amount suitable to obtain the desired weldability. Table 7 shows compositional ranges that would exhibit hot corrosion resistance and improved weldability. It is preferred that the composition consists essentially of only these elements. Also, in one preferred embodiment, the amount of Pt, Hf, Y, and Sc is zero.

Table 7

Element	Range (wt. %)	Preferable Range (wt. %)	Most Preferable Range (wt. %)
Al + Ti	0.5-10	1-9	2-5.5
B	0-0.01	0-0.007	0.006 max
C	0-0.15	0-0.1	0.03 max
Co	0-25	2-20	3-15
Cr	5-30	10-25	12-22
Fe	0-70	0-30	5 max
Hf + Y + Sc	0-0.009	0-0.005	0.005 max
Mo and/or W	0.5-20	1-15	1.5-12
Nb and/or Ta	0-8	0-7	0-5
Ni	0-70	10-68	18-63
Pd	2-50	2-45	5-40
Pd + Ni + Fe	50-72	55-70	58-68
Re and/or Rh	0-10	0-5	0.05 max
V	0-5	0-0.5	0.1 max
Zr	0-0.15	0-0.1	0.005 max

Example 5

The design of a new alloy that maximizes the benefits of the addition of palladium to a superalloy may be the best approach for newly design components or redesign of existing components. The design of a new alloy requires knowledge of the intended application or applications. For gas turbine operating temperatures above about 870°C, oxidation is the dominating mechanism of base metal attack. Therefore a newly designed alloy for this temperature range must be resistant to oxidation. Typically aluminum is added to alloys to increase oxidation resistance via the formation of an Al_2O_3 scale. To improve weldability of these alloys, palladium is added in an amount suitable to obtain the desired weldability. Table

8 shows compositional ranges that would exhibit oxidation resistance and improved weldability. It is preferred that the composition consists essentially of only these elements.

Also, in one preferred embodiment, the amount of Pt, Hf, Y, and Sc is zero.

Table 8

Element	Range (wt. %)	Preferable Range (wt. %)	Most Preferable Range (wt. %)
Al + Ti	1-10	3-9	3-7.5
B	0-0.01	0-0.007	0.006 max
C	0-0.15	0-0.1	0.03 max
Co	0-20	2-15	3-12
Cr	0-20	2-15	3-12
Fe	0-10	0-5	0.5 max
Hf + Y + Sc	0-0.009	0-0.005	0.005 max
Mo and/or W	0.5-20	1-18	1.25-15
Nb and/or Ta	0-10	0-8	0-6
Ni	0-70	4-68	12-60
Pd	2-55	3-52	5-45
Ni + Pd	55-72	56-71	57-65
Re and/or Rh	0-10	0-5	0.05 max
V	0-5	0-0.5	0.1 max
Zr	0-0.15	0-0.01	0.005 max

Example 6

Turbine blade tips are currently repaired using a number of different processes and materials. Repair cost is of primary importance to the engine owner. The most cost effective repair is to use an alloy with excellent weldability and apply a new tip using a manual tungsten-inert-gas welding process. In some cases, a more precise welding process such as plasma transferred arc or laser is used to reduce repair costs. However, as previously described, alloys with excellent weldability lack strength and oxidation resistance. In recent years investigators have tried several methods use advanced alloys as weld fillers. One technique is to preheat the component to be repaired to very high temperatures (400-1100°C). The idea being that the high temperature preheat will reduce cracking. Although this method has limited success it suffers from several problems. One problem is that the high preheat may increase base metal cracking. Another problem is the cost associated with the preheat. Preheating parts requires expensive equipment and extra process controls, often reducing productivity, increasing reject rates. The alloys in this invention can be used to repair

components such as turbine blades, combusters, seals, vanes, and shafts by conventional repair procedures. This is advantageous because no additional equipment is required to use the new alloy. Component repair costs is kept to a low value.

There are several ways the new alloys can be used for repair. One way is to use a
5 weld filler alloys that has a composition based on the original component alloy but modified with Pd (as outlined in Example 1 and 2). Another way is to use a completely new alloy based on the compositions (as outlined in Example 3 and 4).

Although the invention has been described in detail in the foregoing for the purpose of
10 illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

We claim:

1. A Ni, Fe, or Co based superalloy containing from 2-55 wt % Pd such that the total wt % of Ni + Pd is in the range 50-80.

2. A superalloy comprising:

Element	Range (wt. %)
Al + Ti	1-10
B	0-0.01
C	0-0.15
Co	0-20
Cr	0-20
Fe	0-10
Hf + Y + Sc	0-0.009
Mo + W	0.5-20
Nb + Ta	0-10
Ni	0-70
Pd	2-55
Re + Rh	0-10
V	0-5
Zr	0-.015

wherein the wt % of Al is > 0 and the total amount of Pd + Ni lies in the range of 55-72 wt %.

3. The superalloy according to claim 2 comprising

Element	Preferable Range (wt. %)
Al + Ti	3-9
B	0-0.007
C	0-0.1
Co	2-15
Cr	2-15
Fe	0-5
Hf + Y + Sc	0-0.005
Mo + W	1-18
Nb + Ta	0-8
Ni	4-68
Pd	3-52
Re + Rh	0-5
V	0-0.5
Zr	0-0.1

wherein the wt % of Al is > 0 and the total amount of Pd + Ni lies in the range of 56-71 wt %.

4. A superalloy according to claim 2 wherein the atomic ratio of nickel to palladium is about 1:1.

5. A Ni, Fe, or Co based superalloy containing from 2-50 wt % Pd such that the total wt % of Ni + Pd + Fe is in the range 50-80.

6. A superalloy comprising

Element	Range (wt. %)
Al + Ti	0.5-10
B	0-0.01
C	0-0.15
Co	0-25
Cr	5-30
Fe	0-70
Hf + Y + Sc	0-0.009
Mo + W	0.5-20
Nb + Ta	0-8
Ni	0-70
Pd	2-50
Re + Rh	0-10
V	0-5
Zr	0-0.15

wherein the wt % of Al is > 0 and the total amount of Pd + Ni + Fe lies in the range of 50-72 wt %.

7. The superalloy according to claim 6 comprising

Element	Range (wt. %)
Al + Ti	1-9
B	0-0.007
C	0-0.1
Co	2-20
Cr	10-25
Fe	0-30
Hf + Y + Sc	0-0.005
Mo + W	1-15
Nb + Ta	0-7
Ni	10-68
Pd	2-45
Re + Rh	0-5
V	0-0.5
Zr	0-0.1

wherein the wt % of Al is > 0 and the total amount of Pd + Ni + Fe lies in the range of 55-70 wt %.

8. A superalloy according to claim 6 wherein the atomic ratio of nickel to palladium is about 1:1.
9. A turbine blade comprising a superalloy according to claim 1 or 6.

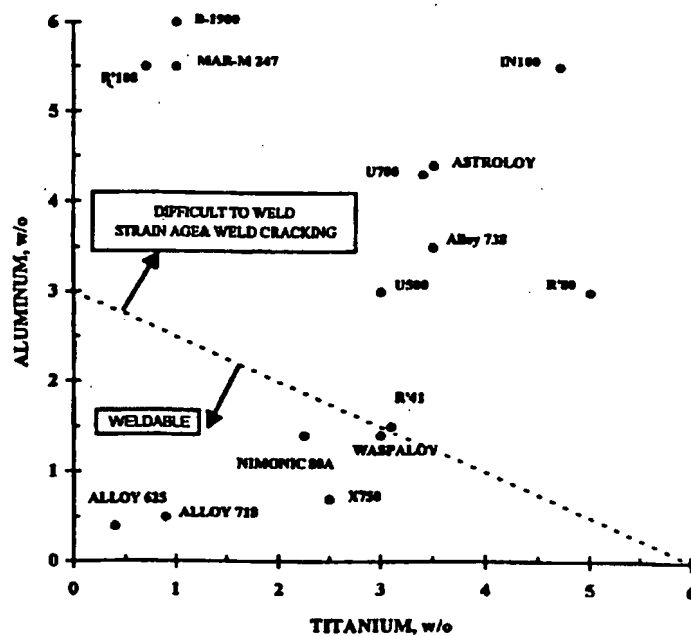
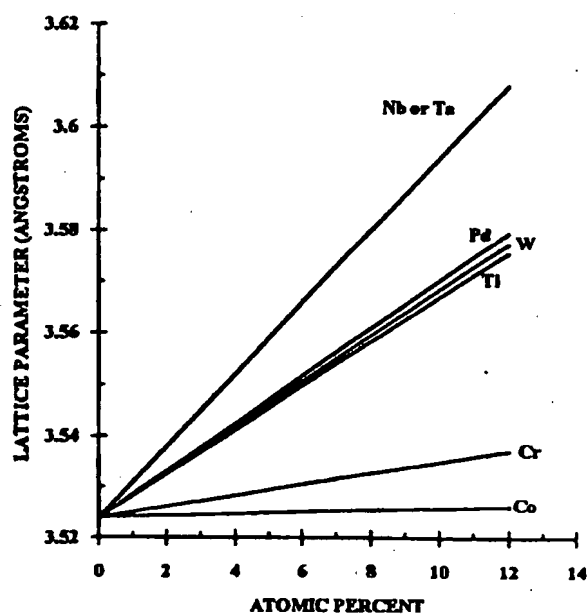
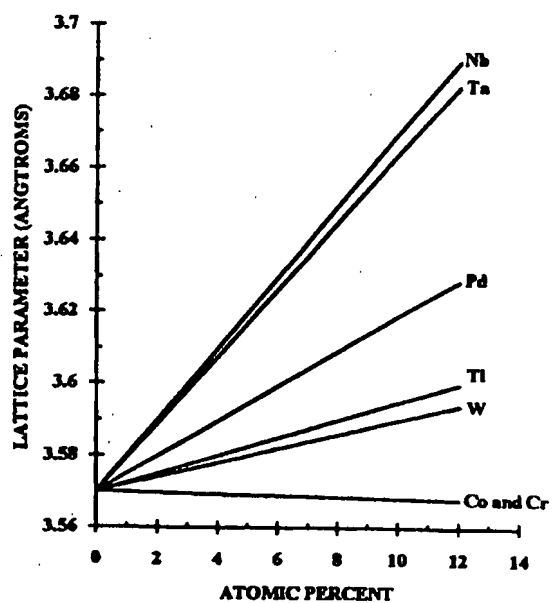
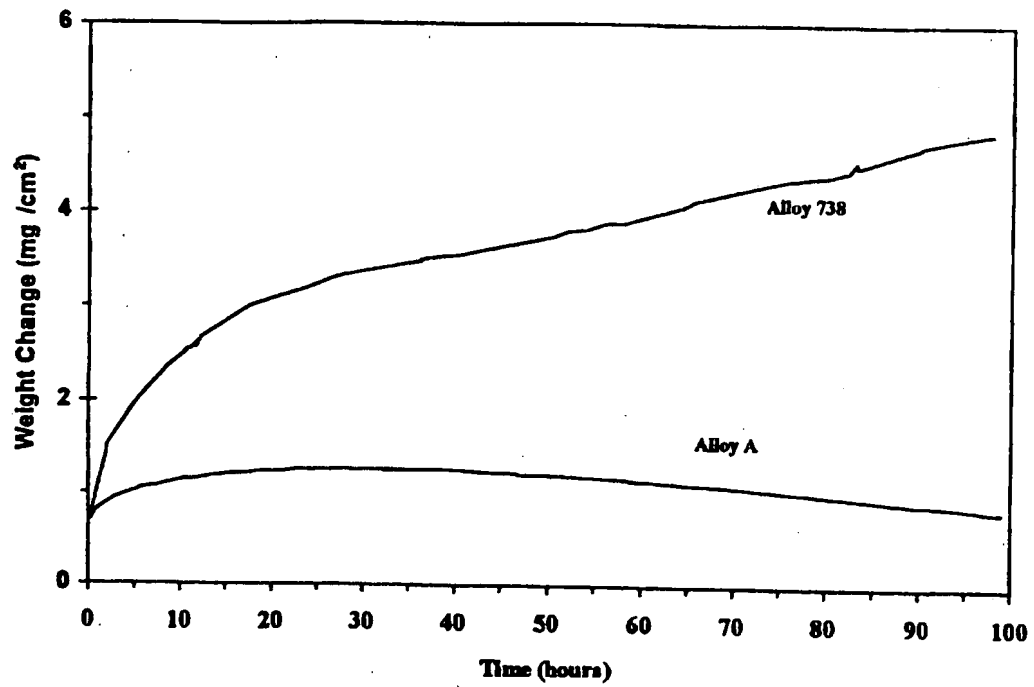
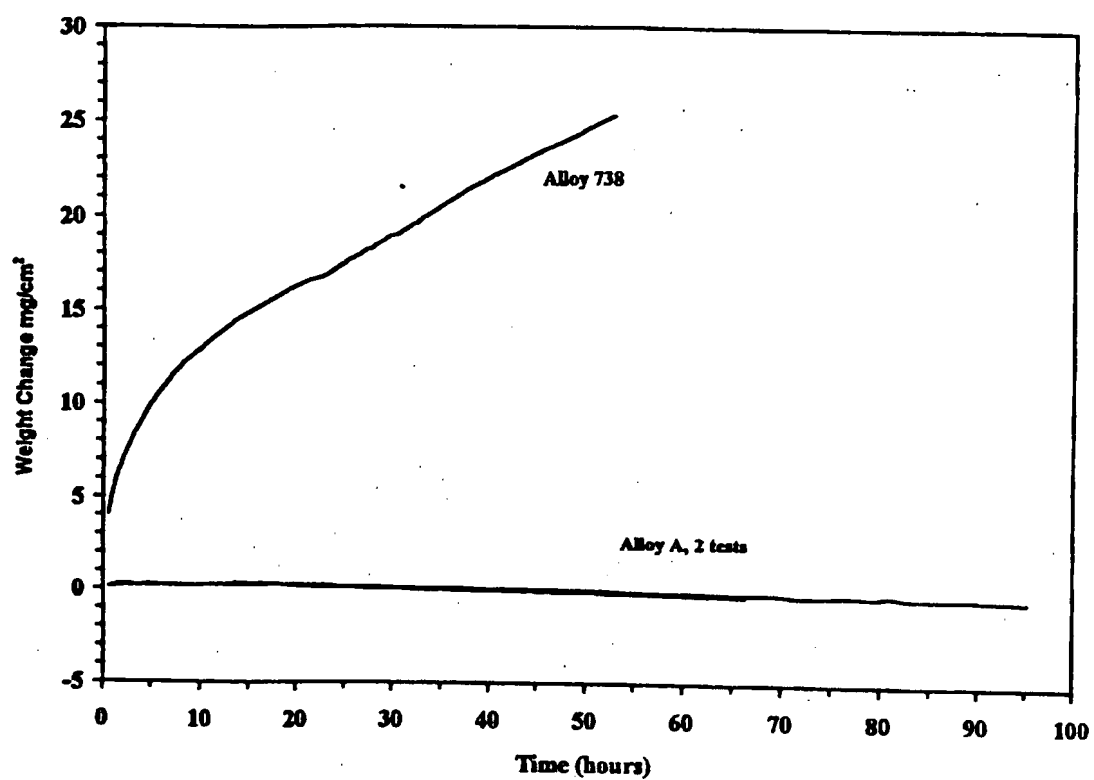


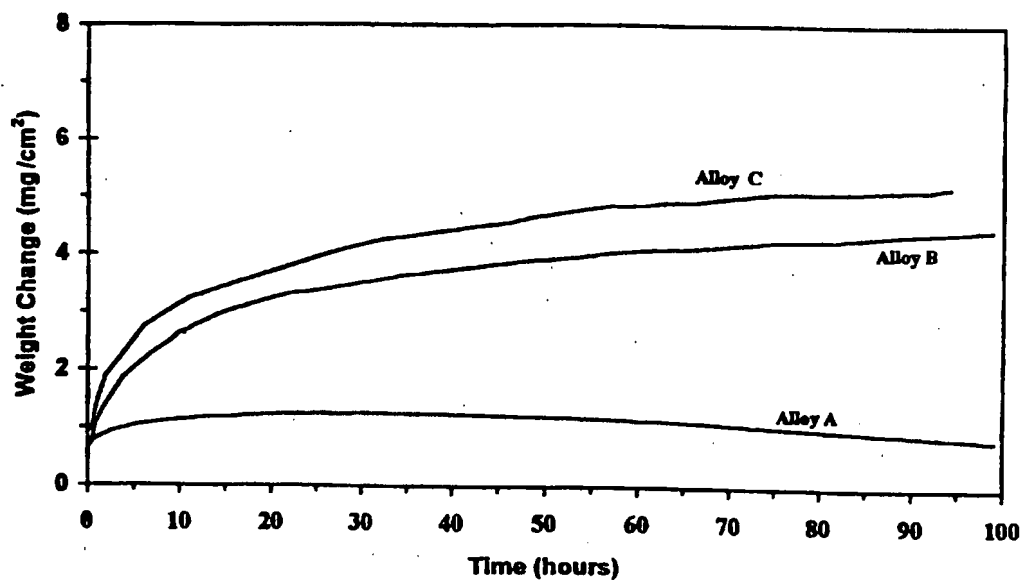
FIGURE 1

**FIGURE 2**

**FIGURE 3**

**FIGURE 4**

**FIGURE 5**

**FIGURE 6**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/05974

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : 420/35,95,97,436,440,443,444; 148/336,408,409,410,419,425,442

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 420/35,95,97,436,440,443,444; 148/336,408,409,410,419,425,442

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,719,080 A (DUHL ET AL) 12 January 1988, abstract, col. 1, lines 11-19; table 1.	1-3, 5-7, 9
Y	US 4,061,495 (SELMAN ET AL) 06 December 1977, abstract, col. 1, lines 15-24, 51-col. 2, line 35; col. 5, lines 10-18.	1-3, 5-7, 9
A	US 4,615,864 A (DARDI ET AL) 07 October 1986, abstract.	

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A document defining the general state of the art which is not considered to be of particular relevance	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* E earlier document published on or after the international filing date	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* L document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* Z	document member of the same patent family
* O document referring to an oral disclosure, use, exhibition or other means		
* P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

05 JUNE 1997

Date of mailing of the international search report

02 JUL 1997

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

MARGERY S. PHIPPS

Telephone No. (703) 308-0648

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/05974

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

C22C 5/04, 19/03, 19/05, 19/07, 30/00, 38/08, 38/10, 38/12, 38/14, 38/18, 38/22, 38/24, 38/26, 38/28, 38/30, 38/32, 38/40, 38/44, 38/46, 38/48, 38/50, 38/50, 38/52, 38/54